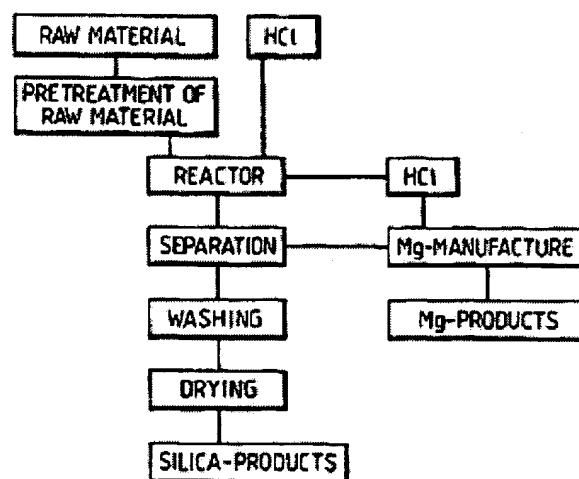


A METHOD FOR MANUFACTURING SPHERICAL SILICA FROM OLIVINE**Publication number:** WO9507235**Publication date:** 1995-03-16**Inventor:** OLERUD SVEIN (NO)**Applicant:** OLERUD SVEIN (NO)**Classification:****- international:** **C01B33/187; C01B33/00;** (IPC1-7): C01B33/187;
C01B33/142**- european:** C01B33/187; Y01N6/00**Application number:** WO1994NO00145 19940901**Priority number(s):** NO19930003168 19930906**Also published as:**EP0720587 (A1)
US5780005 (A1)
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EP0720587 (A0)
BR9407389 (A)

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Cited documents:AT352684B
GB2078703**Report a data error here****Abstract of WO9507235**

In a method for manufacturing silica a leaching of natural silicates is performed with hydrochloric acid or other mineral acids, draining, drying and possibly a grinding up of the residue of the product obtained. In order to obtain a spherical silica with a controlled particle size and surface characteristics a mineral olivine with the highest possible degree of purity is employed as the basic material. This raw material is reduced to a grain size between 0.05 and 5 mm. The particles are pretreated and washed for the removal of dust on the grain surfaces and heavy materials such as spinel and at least a part of the foliar and stem-like minerals such as serpentine, talc and pyroxene are removed. The olivine particles are then leached in a controlled leaching process where the acid concentration, leaching temperature and leaching time are controlled in order to achieve the desired primary particle size, specific surface and pore volume measured according to the BET method on the extracted silica. The particle agglomerate of spherical particles thus formed with a grain size between 30 and 70 nanometres are washed and dried in the conventional manner, whereupon the agglomerate is divided into the spherical particles.

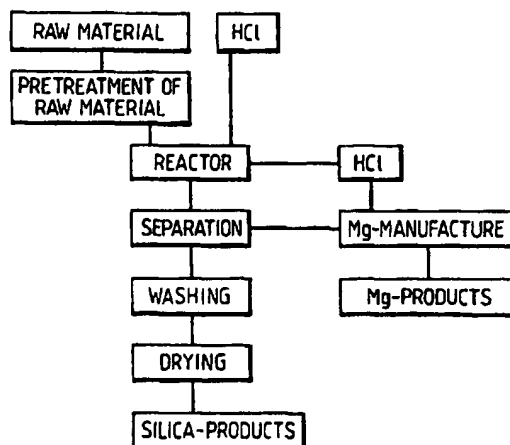


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(54) Title: A METHOD FOR MANUFACTURING SPHERICAL SILICA FROM OLIVINE**(57) Abstract**

In a method for manufacturing silica a leaching of natural silicates is performed with hydrochloric acid or other mineral acids, draining, drying and possibly a grinding up of the residue of the product obtained. In order to obtain a spherical silica with a controlled particle size and surface characteristics a mineral olivine with the highest possible degree of purity is employed as the basic material. This raw material is reduced to a grain size between 0.05 and 5 mm. The particles are pretreated and washed for the removal of dust on the grain surfaces and heavy materials such as spinel and at least a part of the foliar and stem-like minerals such as serpentine, talc and pyroxene are removed. The olivine particles are then leached in a controlled leaching process where the acid concentration, leaching temperature and leaching time are controlled in order to achieve the desired primary particle size, specific surface and pore volume measured according to the BET method on the extracted silica. The particle agglomerate of spherical particles thus formed with a grain size between 30 and 70 nanometres are washed and dried in the conventional manner, whereupon the agglomerate is divided into the spherical particles.

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A method for manufacturing spherical silica from olivine

The invention concerns a method for manufacturing silica in the form of spherical particles with a low content of iron and impurities, by leaching natural silicates with the use of hydrochloric acid or other mineral acids in a reactor, and then separating, washing, drying and possibly grinding up the silica, that the raw material used is mineral, preferably monovalent mineral olivine with the highest possible degree of purity, that the raw material is reduced to a particle diameter between 0.05 and 5 mm, preferably 0.1 and 0.5 mm.

Silica is generally employed as a filling material over a wide range of products and over an extensive range of applications. In order to achieve the best possible effect as a filling material it is therefore important for it not only to have adequate purity and whiteness, but that it should be possible to vary the specific surface and pore volume. Substances regarded as impurities in this context are mineralogical particles, ionic deposits and the like. This is of vital importance for the filler's adsorption properties, viscosity-regulating properties, abrasion and refraction properties. It is also important to be able to control the particle size and surface characteristics, thus enabling control to be retained over the introduction of fillers into a product and their effect. In this connection it will be advantageous to be able to manufacture silica in spherical form and with a defined size.

The object of the invention is to provide a method for the manufacture of the silica which satisfies the above-mentioned requirements, i.e. a spherical silica with a controlled particle size and surface characteristics. This silica has characteristics corresponding to precipitated silica which has a number of applications as a filler. These products are manufactured from potassium silicate and sulphuric acid. The object of the invention is to develop an alternative process with olivine as a raw material which provides corresponding products.

This object is achieved with a method which is characterized by the features in the patent claims presented.

By means of the invention the surprising discovery has been made that silica prepared from olivine can be formed in the shape of spherical primary particles with a diameter of 30-70 nanometres (10^{-9} m). The particles which are extracted by the method according to the invention will be an agglomerate of primary

particles which easily disperse in liquids. By means of the invention it has further been discovered that the silica's primary particle size, its specific surface and pore volume, measured according to the BET method, can be adjusted depending on the leaching time, the temperature and acid concentration used in the process. This fact makes it possible by means of the method according to the invention to give the spherical silica particles the desired properties, which are adapted to suit the respective purposes.

For the basic material use is preferably made of crushed olivine, $(\text{Mg}_{1.85}, \text{Fe}_{0.15})\text{SiO}_4$ from the most monovalent possible natural mineral deposits. By the admixture of a mineral acid, e.g. HCl , H_2SO_4 , HNO_3 , the olivine dissolves and forms a green liquid consisting of the acid's anions and cations which are released from the olivine (Mg^{2+} , Fe^{2+} , Ni^{2+}). In addition a residue of solid material is obtained which is a colloidal amorphous silica (SiO_2) in the form of a gel. The silica is separated from the liquid by pressure filters, washed clean of acid remains, dried and ground. A white powder is thus obtained which consists of amorphous silica in the form of primary particles which form larger particle agglomerates. The primary particles will have obtained a spherical shape and a diameter of 30-70 nanometres. The material has a large specific surface ($100\text{-}450 \text{ m}^2/\text{g}$), a large pore volume ($0.7\text{-}1.7 \text{ cm}^3/\text{g}$) and thus a high degree of porosity. The process can be controlled in such a manner that the desired surface and/or pore volume can be obtained.

After crushing or grinding this product will be able to be employed as a filler, viscosity-regulating medium, as an admixture in concrete, etc.

The leached liquid can be used as a raw material for the manufacture of chemicals which contain magnesium, nickel and/or cobalt. The mineral olivine has a content of approximately 30% magnesium and up to 0.3% nickel which dissolves and thus can also be recovered. In the extraction of magnesium metal or magnesium oxide, e.g., the chlorine from the process can be recovered by leaching with hydrochloric acid, converted to hydrochloric acid and recycled.

As already mentioned in the method olivine is used from the most monovalent mineral deposits possible. It is essential to use pure olivine and not olivine which has been converted, e.g., to serpentine, talc and the like.

From Austrian patent no. 352 684 there is previously known a method for extracting silica from serpentine, which also provides silica with large surfaces. This method gives silica particles which have approximately the same shape after the leaching as they had before the leaching. Porous mineral particles are
5 obtained in which the magnesium oxide and iron oxide have been removed from their previous places in the mineral lattice. Thus the material has to be ground down in order to be used and in order to obtain a fine fraction several crushing processes and large amounts of energy have to be employed. Nor is it possible to obtain particles with a grain size as small as 30-70 nanometres by means of
10 ordinary crushing processes. In this process the BET values for the extracted silica are dependent on the grain size of the raw material. The highest BET value is obtained when the raw material which is a serpentine has a grain size between 1 and 3 mm.

Furthermore in Norwegian patent no. 160 200 a method is described for
15 manufacturing active silicon dioxide, derived from natural silicates. The extracted material is subjected to a separation process by means of wet separation methods for separating insoluble parts and heavy soluble parts such as olivine. This shows that for this process other natural silicates than olivine have preferably been employed.

20 Norwegian patent no. 143 583 describes a method for leaching the metal content in naturally occurring silicates. In order to obtain the greatest possible yield from the leaching of the metal content it has been found that it is advantageous for the grain size of the basic material to be between 0.3 and 5 mm. As a by-product the process provides a residue which mainly consists of silicic acid.
25 Contaminated silicic acid cannot be used for most silica products given present day requirements.

JP-60161320 specifies a method for manufacturing silica gel from particles of a natural silicate mineral such as, e.g., olivine. The particles are treated with acid and washed.

30 The invention will now be described in more detail by means of embodiments and figures which illustrate:

- Fig. 1 is a process diagram for the method according to the invention, and
- figs. 2 and 3 are diagrams illustrating the invention.

Fig. 1 of the drawing is a process diagram illustrating a method for manufacturing chemically precipitated silica by treating olivine with acid. The process is designed in order to give the silica the best possible quality. The diagram illustrates the main principle involved in the manufacture of silica and magnesium products on the basis of olivine and hydrochloric acid, but other mineral acids such as sulphuric acid and nitric acid act in a similar manner.

Olivine of the purest possible quality should be used since most other minerals will not dissolve when treated with acid and will thus represent a possible contamination of the silica product. Most other minerals will end up as solid waste from the process. The olivine which is used is crushed and sifted as a sand fraction. Commercially available Norwegian olivine consists, e.g. of:

olivine	90-95 weight percent
pyroxene, serpentine	5 weight percent
spinel	1 weight percent
chlorite	1,5 weight percent

This olivine has a forsterite content of 92% (92 mol percent forsterite, 8 mol percent fayalite), i.e. approximately 50 weight percent MgO.

Partially serpentinized olivine stone will not provide satisfactory products.

Pretreatment of the olivine sand can be performed by gravitative separation (wash table, spirals or the like) and sifting in order to obtain the desired grain sizes between 0.05-5 mm, preferably 0.1-0.5 mm.

The object is to wash away dust particles on the grain surfaces since the small particles which are not olivine will end up in the silica product as contamination after and leaching and separation. In addition heavy minerals such as spinel and some of the foliar and stem-like minerals such as serpentine, talc and pyroxene should be removed before the leaching process in order to reduce the consumption of acid.

Table 1 illustrates an example of the chemical composition of olivine from two different Norwegian deposits before and after treatment with wash table where a

heavy mineral fraction and a fine fraction of light, fine-grained and foliar minerals have been separated. Table 1 illustrates that the content of MgO, Ni, and Co increase with this purification process, this being desirable since these elements dissolve during the leaching process and can be extracted from the solution. The Al O content is substantially reduced, which indicates that most of the pyroxene has been removed, which is clearly desirable. The silica content is somewhat reduced, but this is desirable in this case as this silica is bonded to non-soluble silicates such as pyroxene, serpentine and talc.

Table 1

Analyses of olivine sand

Main elements in %

	Sample 1		Sample 2	
	Before	After	Before	After
SiO ₂	42,29	41,33	41,86	41,82
Al ₂ O ₃	0,81	0,06	0,70	0,39
Fe ₂ O ₃	6,1	7,36	7,71	7,92
TiO ₂	<0,01	<0,01	0,03	0,01
MgO	47,87	49,68	48,41	49,19
CaO	0,04	0,05	0,41	0,34
Na ₂ O	<0,1	<0,10	0,19	<0,01
K ₂ O	<0,01	<0,01	0,03	0,01
MnO	0,09	0,10	0,10	0,11
P ₂ O ₅	<0,01	<0,01	<0,01	<0,01
Ignition loss	1,34	0,11	0,48	0,17
Total	98,54	98,69	99,93	100,00

Trace elements in ppm:

Zn	43	35
Cu	7	8
Ni	2700	3000
Cr	3600	813
Co	113	135

Table 2 illustrates chemical data for precipitated silica from pretreated olivine and non-pretreated olivine.

Table 2

Analyses of precipitated silica products

	(pretreated olivine)	(non-pretreated olivine)
SiO ₂	90,87	90,49
Al ₂ O ₃	<0,01	0,02
Fe ₂ O ₃	0,02	0,06
TiO ₂	<0,01	<0,01
MgO	0,16	0,32
CaO	0,01	0,03
Na ₂ O	<0,10	<0,10
K ₂ O	<0,01	<0,01
MnO	<0,01	<0,01
P ₂ O ₅	<0,01	<0,01
Ignition loss	0,17	0,48
Total	99,30	99,09

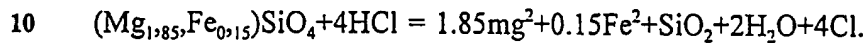
15 Technical data for precipitated silica of pretreated olivine.

Specific surface	108 m ² /g Measured with the BET method
Specific pore volume	1,55 cm ³ /g Measured with the BET method
Particle density	0,47 g/cm ³ Measured with the BET method
Material density	2,1 g/cm ³ Pycnometer measurement
Porosity	73%
Primary particle size	30-70 nm SEM test
Bulk density	0,17 g/cm ³
Whiteness FMX	94,5% Standard whiteness measurement
Whiteness FMY	94,4% Standard whiteness measurement
Whiteness FMZ	94,6% Standard whiteness measurement
Whiteness R457	94,6% Standard whiteness measurement

Table 2 also illustrates the chemical difference between the products in the form of a lower content of Al, Fe, Mg and Ca after treatment. The Fe content in particular is a decisive factor for the whiteness and thereby the quality as a filler.

Technical data also shows that the whiteness from silica which is not pretreated is 4% lower.

Acid is added to the crushed olivine in a reactor with heating and continuous stirring or a reactor of the countercurrent type. The treatment in the acid bath is crucial for determining which silica product is obtained, and the variables here are acid strength, time in the reactor, temperature and grain size of the olivine. Experiment shows that 6N acid of HCl and H₂SO₄ give optimum solubility. After several intermediate steps, the main reaction when using hydrochloric acid is:



Experiments have been conducted with regard to control of the leaching process. Experiments with 4 different variables in the leaching process give results which correspond to those which were specified in table 1 above. The experiments were performed with varying time, varying temperature, varying acid strength and varying grain size. The experiments were conducted in a laboratory with glass flasks with heating and continuous stirring with a magnetic rotor. The olivine was splashed up in the flask when the acid was boiling. After leaching for a specified time the liquid was poured directly into a centrifugal glass and centrifuged and washed to a pH value of 6. The samples were then dried in a drying cabinet at 110°C. The solubility of olivine varies greatly in the different experiments. The consistency of the silica gel after leaching in the reactor and in the dried product gives a good indication of the specific surface. Gel with high surfaces is transparent, while lower surfaces are white. After drying hard lumps of gel are formed with a specific surface over approximately 300 m²/g, an intermediate group is in the area of 250-300 m²/g, while samples with under approximately 250 m²/g give a loose, airy powder. The specific surface is determined by means of the BET method, see table 3.

Figs 2 and 3 plus table 3 below illustrate the correlation between the different variables and specific surfaces. The conclusions are:

1. Increasing time in the reactor give a decreasing specific surface and increasing pore volume.
2. Stronger acid give decreasing specific surface and increasing pore volume.
3. Increasing temperature gives decreasing surface and increasing pore volume.
4. The correlation between grain size and specific surface is not unambiguous.

On the basis of these findings it has been possible to establish that the control of the leaching process based on the above criteria can predict specific surface and pore volume for the product.

- 5 Precipitated silica can be industrially separated from the acid bath with pressure filters. Several qualities can be industrially separated from one another with cyclones. The separation is relatively simple since most of the "contaminated" particles of other mineral grains, which are unaffected or only partially affected by the acid treatment are heavier or larger than the primary silica particles and it will therefore be possible to separate them by means of gravitative separation.

Table 3

No.	time	temp. °C	grain size	acid strength	Spec. surface m ² /g	Pore volume ml/g	Pore diameter Å	consistency
641	10 min	110	0,5 mm	6N	331	1,14	230	hard lumps
642	20 min	110	0,5 mm	6N	292	1,29		hard lumps
643	40 min	110	0,5 mm	6N	211	1,34		loose powder
644	2 h	110	0,5 mm	6N	173	1,35		loose powder
645	4 h	110	0,5 mm	6N	152	1,39		loose powder
646	2 h	53	0,5 mm	6N	319	1,10		hard lumps
647	2 h	90	0,5 mm	6N	197	1,35		loose powder
648	20 min	110	0,18 mm	3N	450	0,95	100	hard lumps
649	2 h	110	0,5 mm	3N	403	1,19	150	hard lumps
650	2 h	110	0,5 mm	8N	120	0,74		loose powder
651	3 min	110	0,18 mm	6N	269	1,31	300	hard lumps
652	20 min	110	0,18 mm	6N	267	1,66		medium hard
653	40 min	110	0,18 mm	6N	235	1,50		medium hard
654	2 h	110	0,5 mm	3N*	427	1,00	110	hard lumps
	20 min	110	0,5 mm	3N				too low solubility
	2 h	110	0,5 mm	1,5N				too low solubility
	2 h	26	0,5 mm	6N				too low solubility

*1/10 quantity of acid.

Carrier for sprays.

Admixture for paper pulp.

Anticaking and free-flow agents.

Antiblocking agents.

5 Admixture for toothpaste, thickening and polishing agents.

Admixture in concrete (pozzolan).

Fireproof materials.

Raw materials for silicones, silanes, etc.

10 Silica manufactured according to the invention will naturally also be able to be
used for other purposes than that described above if this is advantageous.

Washing of silica in order to remove acid remains is repeated until the salts have been removed and the desired pH has been achieved for the product. This can be done industrially with pressure filters, where water is added to the filter cake between each filtration.

- 5 Drying produces a white, light crust whose consistency will vary with the specific surface. High specific surfaces produce hard lumps which have to be ground down, low specific surfaces produce a loose powder which does not require grinding.

Grinding to the desired particle size can be performed according to requirements.

- 10 The chemical and physical data (table 2) for precipitated silica produced by acid treatment of olivine corresponds to what is normally described internationally as precipitated silica. These products are made of potassium silicate (Na_2SiO_3) to which is added an acid (usually sulphuric acid) and reacts to colloidal silica which is then washed, dried and ground down to the desired aggregate size. By
15 preparing precipitated silica directly from olivine it is not necessary to use potassium silicate which is normally made from quartz (SiO_2) and Na_2CO_3 at approximately 1400°C or from quartz and $\text{Na}(\text{OH})$ at $150\text{-}200^\circ\text{C}$ and high pressure.

- 20 Production costs will be lower in the olivine-based process than in the traditional one since:

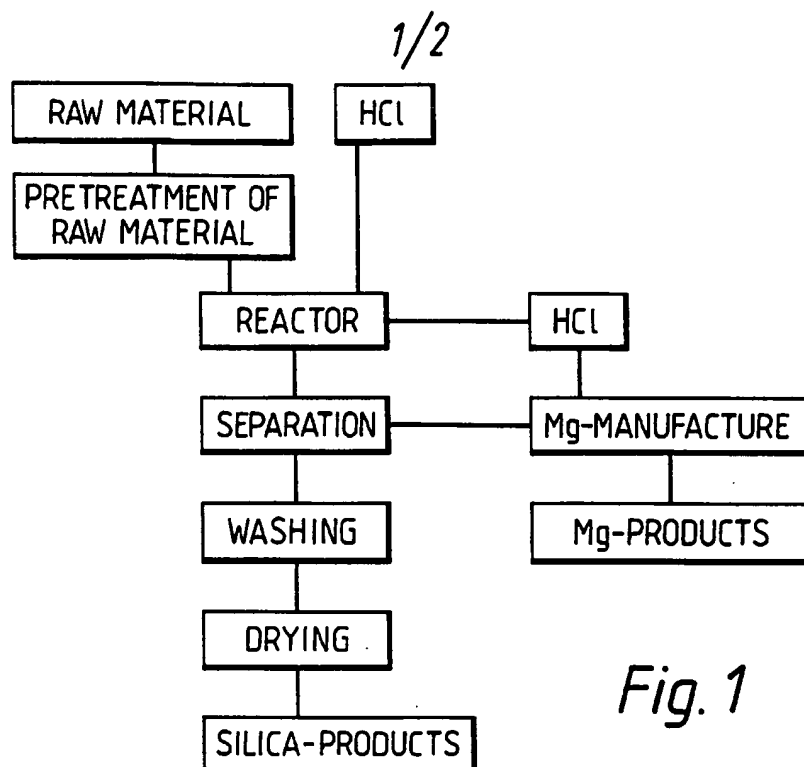
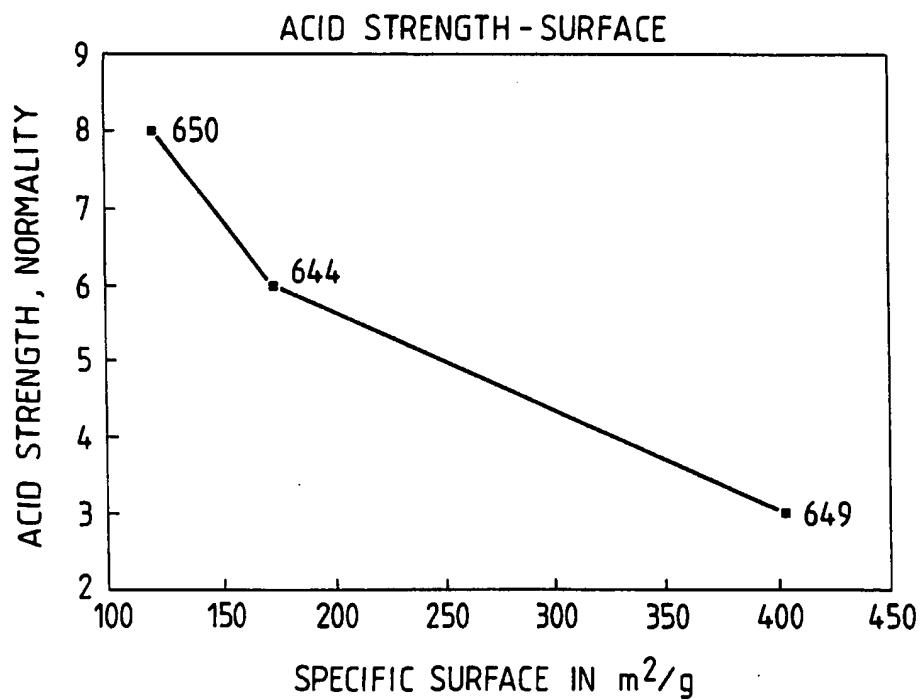
- 25 The energy consumption is lower for manufacturing the product. Olivine is considerably cheaper as a raw material than potassium silicate which is made from quartz, bicarbonate of soda and/or sodium hydroxide. A combination of a process which chemically utilizes the leached Mg and possibly Ni in the olivine, and which can recycle the mineral acids used will be financially and environmentally favourable.

Spherical silica obtained by the method according to the invention can be used in many different ways. The most advantageous areas of application are listed below:

- 30 Filler in rubber and plastic.
 Filler, thickener in paint.
 Filler, thickener in glue and putty.

PATENT CLAIMS

1. A method for manufacturing silica in the form of spherical particles with a low content of iron and impurities, by leaching of natural silicates with hydrochloric acid or other mineral acids in a reactor, then separating, washing, drying, and possibly grinding up the silica, that as a raw material mineral, preferably monovalent mineral olivine is used with the highest possible degree of purity, that the raw material is reduced to a particle diameter between 0.05 and 5 mm, preferably 0.1 and 0.5 mm, characterized by the following steps:
- 10 - the raw material is pretreated and washed for the removal of dust on the particle surfaces,
 - the raw material's heavy minerals, such as spinel and at least a part of the foliar and stem-like minerals such as serpentine, talc and pyroxene, are removed according to known per se methods,
 - 15 - the olivine particles are then leached in a reactor where acid concentration, leaching temperature and leaching time are varied in order to obtain the desired specific surface measured according to the BET method on the extracted silica (figs. 2 and 3),
 - the particle agglomerate of spherical particles thereby formed with particle sizes between 30 and 70 nanometres are washed and dried in the conventional manner.
 - 20
2. A method according to claim 1, characterized in that as a raw material olivine with the following composition is used:
- | | | | |
|----|--------------------------------|-------|-----------------|
| 25 | SiO ₂ | 30-43 | weight percent |
| | Fe ₂ O ₃ | 0-70 | weight percent |
| | MgO | 0-57 | weight percent |
| | Ni | 0-0.5 | weight percent |
| | Ignition loss | 0-5 | weight percent. |

*Fig. 1**Fig. 3*

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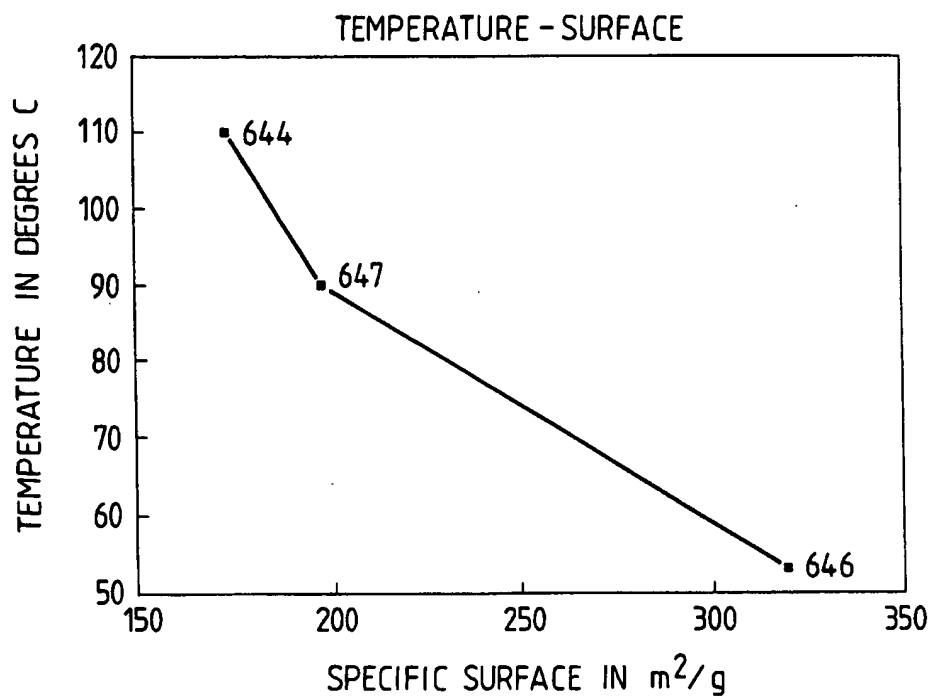
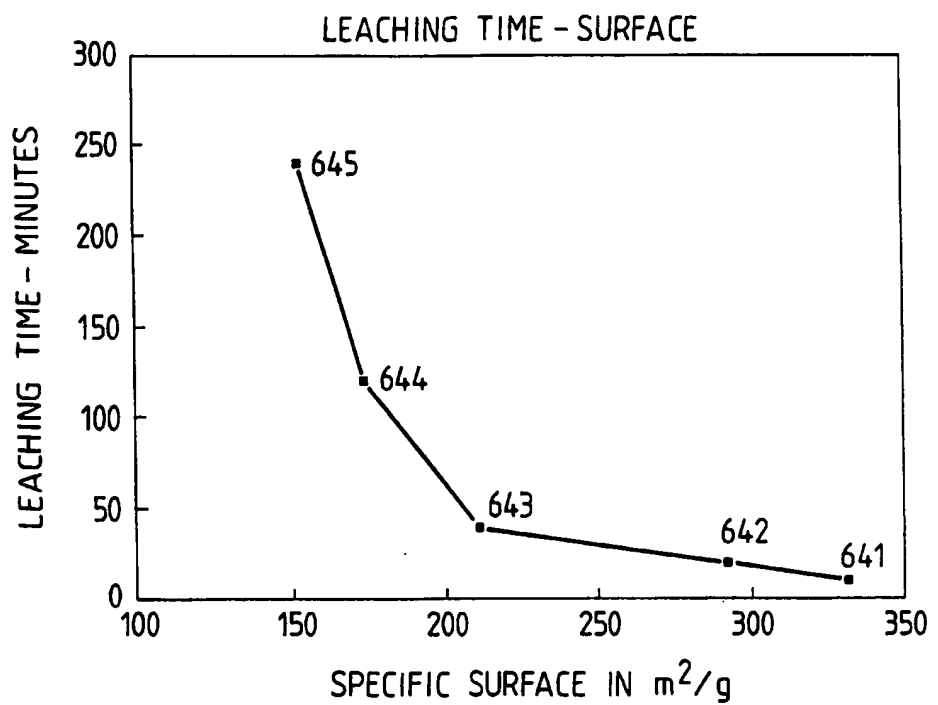


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 94/00145

A. CLASSIFICATION OF SUBJECT MATTER		
IPC6: C01B 33/142 // C01B 33/187 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
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DIALOG: WPI, CLAIMS		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AT, B, 352684 (STEIRISCHE MAGNESIT-INDUSTRIE AKTIENGESELLSCHAFT), 10 October 1979 (10.10.79), page 2, line 21 - line 35 --	1-2
A	GB, A, 2078703 (STEIRISCHE MAGNESIT-INDUSTRIE AG), 13 January 1982 (13.01.82), page 1, line 14 - line 28 -- -----	1-2
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INTERNATIONAL SEARCH REPORT
Information on patent family members

29/10/94

International application No.

PCT/NO 94/00145

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
AT-B-	352684	10/10/79	DE-A,C-	2625868	23/12/76
			GB-A-	1488339	12/10/77
GB-A-	2078703	13/01/82	AT-A-	377958	28/05/85
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